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(4-Vinylpyridine-Styrene) Copolymer as Host Polymer for Chromophoric Complexes with Potential Second Order Nonlinear Optical Properties

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Summary: A series of new metal containing polymers for second order nonlinear optics have been prepared by grafting Cu (II) and Pd (II) chromophoric complexes on a preformed (4-vinylpyridine-styrene) copolymeric backbone. The metallated polymers have been chemically and physically characterized. They show high glass transition temperatures, high thermal stability and good solubility. Their properties have been compared with analogous metallated poly(4-vinylpyridine) samples: variations in the polymeric backbone, as well as in ligands, metal, and metallation ratio, allow to tune their properties.

Keywords: chromophoric metal complexes; grafted polymers; metal-polymer complexes; NLO; polymers

Introduction

Recently we reported[1] a new kind of metallated polymers for non linear optics, obtained by coordination of palladium (II) and copper (II) chromophoric fragments to the donor pyridinic nitrogen of preformed (and commercially available) poly(4-vinylpyridine) (PVP). It was observed that the grafted polymers display some remarkable properties: high glass transition temperatures (higher than the free polymeric backbone), high thermal stability and good solubility. Polymer thin films obtained by the spin-coating technique were transparent and homogeneous. The peculiar nature of the interaction between the chromophores and the polymeric backbone, i.e. the coordination bond from the polymeric chain to the metal, allows us to consider them in between the covalently bonded side-chain type polymers and the guest-host systems. So, some mobility can

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be expected through complexation-decomplexation equilibria at temperature higher than the glass transition temperature, positively affecting the efficiency and stability of poling order.[1] Another advantage of these systems is the possibility to separate the polymerization steps from the insertion of the NLO active units, thus avoiding the problem of functionalizing the dyes. Moreover, some properties of the NLO polymeric materials, such as molecular weights and chromophores concentration, can be tuned more easily. At the same chromophore ratio, some properties of the materials (i.e. glass transition temperature, viscosity, NLO response) can be modified by changing the metal or the ligands or the polymeric backbone.

Here we report a series of preliminary results aiming at checking the effect of changes in the host polymeric matrix on the final material properties, with regard to the analogous group of PVP based materials. For this aim we have prepared a 4-vinylpyridine-styrene copolymer (VPyS) and a 4-vinylpyridine-methyl methacrylate copolymer (VPyMMA) (see Figure 1) to be used as preformed host backbones.

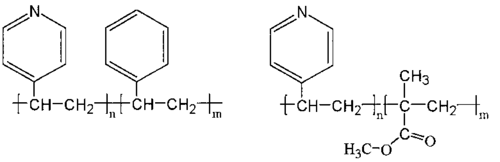


Figure 1. Formulae of VPyS and VPyMMA random copolymers.

Using a copolymeric matrix affords the advantage of reducing the number of free pyridinic groups in the grafted material. In fact the hydrophilic free pyridine groups could make the polymer hygroscopic: moisture could inhibit or cause the loss of the poling order.

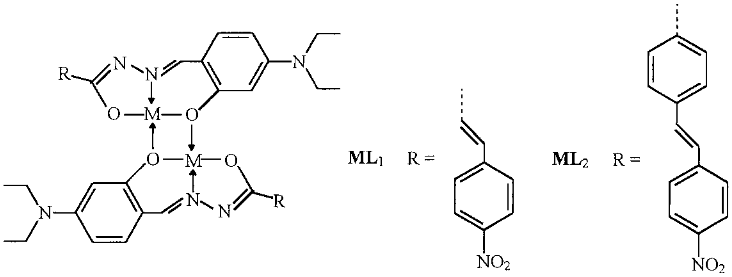
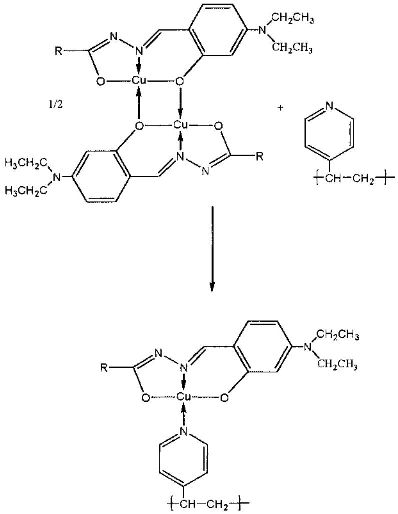


Figure 2. Structure of the complexes ML_1 and ML_2.

Grafted PVP samples containing the fragment ML_1 have been already synthesized and characterized by us.[2] The corresponding chromophores display quite good NLO properties. EFISH measurements[2, 3] on model complexes related to ML_1 and ML_2 (i.e. obtained by coordination of the fragments ML_1 and ML_2 to the donor nitrogen of pyridine) gave respectively 1025 and $1300 \cdot 10^{-48}$ esu, when M=Cu(II), and $1500 \cdot 10^{-48}$ esu, in both cases when M=Pd(II) (at λ = 1907 nm).

The general procedure to insert the complexes on the host copolymer is the same followed to obtain the metallated PVP[1, 2] samples. The starting compound is always a dinuclear centrosymmetric complex[2, 3] of general formula $(M)_2(L)_2$. The synthetic procedure for the PVP CuL series is summarized in Scheme 1.



Scheme 1. Synthesis of metallated Cu(II) PVP from the dinuclear species.

Synthesis

PVP matrix, styrene, 4-vinylpyridine and methyl methacrylate monomers and the initiator α,α'-azobisisobutyronitrile (AIBN) were purchased by Aldrich. VPyS and VPyMMA copolymers were prepared following the same synthetic procedure, setting molar ratio VPy/S=1 and VPy/MMA=1. Below it is described, as an example, the synthesis of VPyS.

Synthesis of VPyS. In a vial 15.8 g of 4-vinylpyridine (0.15 mol) and 15.6 g of styrene (0.15 mol) were mixed with 0.117 g of AIBN and 15 ml of dry DMF. The vial, degassed three times using the freeze-and-thaw technique, was sealed under vacuum and kept at 70 °C for 48 h. The product was recovered by pouring the solution in 400 ml of water, after diluting it with 100 ml of warm (80 °C) DMF. The rubber-like product precipitated was recovered by filtration, dried at 100 °C, then washed several times with hexane and dried at 60 °C. The polymer was purified by dissolving it in 200 ml of dichloromethane and precipitating it in 600 ml of hexane.

The synthetic procedure of the metallated polymers was the same for all the samples, independently of the nature of the metal, the ligand, the polymeric backbone, and the chromophores ratio. Below, as an example, is described the synthesis of the 35% grafted polymers.

Synthesis of VPyS $ML_1$35, VPyS $ML_2$35, PVP $ML_2$35. 0.350 g of the corresponding dinuclear complex and 0.650 g of the anhydrous (obtained by drying at 120 °C for 24 h) polymeric matrix were dissolved in 30 ml of DMF and the solution was heated at 110 °C. After 15 minutes the warm solution was poured in 200 ml of water, containing 2.0 g of sodium acetate. The product was recovered by filtration and washed three times with water, then dried at 120 °C. The yield is substantially quantitative.

Characterization

Polymers were characterized by DSC (Perkin Elmer Pyris), polarizing microscopy (Zeiss Axioskop polarizing microscope equipped with a Mettler FP90 microfurnace), X-ray diffraction (flat film camera, CuKα Ni-filtered radiation), thermogravimetric analysis (TA Instruments SDT 2960 Simultaneous DSC-TGA), UV-Visible spectroscopy (JascoV-560) and ^{1}H NMR spectrometry (Varian Gemini HL 200 MHz and 300 MHz). The inherent viscosities were measured with an Ubbelohde viscosimeter on 0.500 g/dL sample.

Results and Discussion

Very close values of the glass transition temperatures are detected for VPyS (131 °C) and for VPyMMA (135 °C) by DSC analysis (see Figure 3). However, VPyMMA shows clearly a thermal stability lower than VPyS (the decomposition temperatures, calculated at 5% weight loss, are respectively 290 °C for VPyMMA and 354 °C for VPyS).

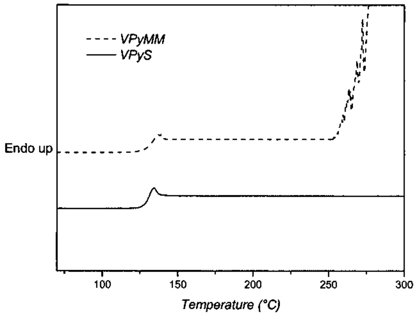


Figure 3. DSC curves of VPyMMA and VPyS.

The higher thermal stability of VPyS justifies our choice to use it as host matrix. The ^{1}H NMR spectra of a sample, respectively, of VPyS and PVP in CD_2Cl_2 and of polystyrene (PS) in $CDCl_3$ are reported below in Figure 4.

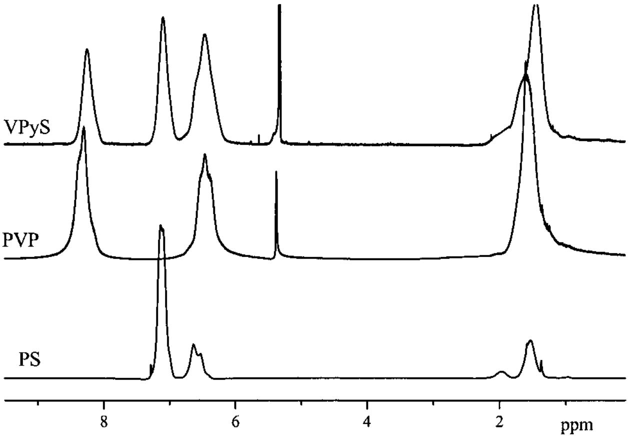


Figure 4. ^{1}H NMR spectra of VPyS, PVP and PS.

As expected[4] the protonic spectrum of the 4-vinylpyridine-styrene copolymer is equivalent to the sum of the spectra of the two homopolymers. The real composition of VPyS has been evaluated by using the method developed by Petit[4]. Comparing the areas of the peaks at 6.4 e 7.1 ppm, correspondent respectively to the two *orto* protons of the two monomeric units and to the *meta* and *para* protons of the styrene units with the area of the signal at 8.3 ppm of the *meta* protons of 4-vinylpyridine units. On the basis of this procedure, we can estimate the real composition as 55% of 4-vinylpyridine and 45% of styrene units. The molecular weight has been measured by a SEC apparatus on THF solutions using a sample of commercial polystyrene as standard. The average molecular weight of VPyS is: M_w=49200; M_n=38000 (dispersion index=1.29).

The most relevant characterization data of the grafted polymers are reported in Table 1 for the PVP samples and in Table 2 for the VPyS samples.

Table 1. Most relevant data for the grafted PVP samples.

	PVP CuL_x					
	$T_g(°C)^a$	$T_d(°C)^b$	$\eta_{inh}(dL/g)^c$	*Molar ratio*^{d}	$CuO_{calc.}{}^e$	$CuO_{exp.}{}^f$
PVP	*147*	*340*	*0.28*	-	-	-
CuL$_1$35*	*192*	*300*	*0.12*	*0.130*	*6.0*	*6.4*
CuL$_2$35	*194*	*300*	*0.15*	*0.110*	*5.3*	*5.8*
CuL$_1$60*	*217*	*301*	*0.09*^{i}	*0.360*	*10.8*	*10.6*
CuL$_2$60	*239*	*311*	*0.08*^{i}	*0.306*	*9.2*	*9.6*
	PVP PdL_x					
	$T_g(°C)^a$	$T_d(°C)^b$	$\eta_{inh}(dL/g)^c$	*Molar ratio*^{d}	$\%Pd_{calc.}{}^g$	$\%Pd_{exp.}{}^h$
PVP	*147*	*340*	*0.28*	-	-	-
PdL$_1$35*	*191*	*348*	*0.27*	*0.118*	*7.7*	*7.7*
PdL$_2$35	*194*	*334*	*0.23*	*0.088*	*6.6*	*6.9*
PdL$_1$60*	*227*	*323*	*0.18*	*0.328*	*13.1*	*13.2*
PdL$_2$60	*220*	*325*	*0.16*	*0.283*	*11.4*	*11.1*

[a] Glass transition temperature; [b] 5% Weight loss temperature; [c] Inherent viscosity measured in DMF at 25 °C and 0.500 g/dL concentration; [d] Molar ratio for metal complex fragments referred to pyridine groups; [e] Calculated metal content as CuO; [f] Found metal content as CuO; [g] Calculated metal content as Pd(0); [h] Found metal content as Pd(0); [i] Inherent viscosity measured in DMF at 60 °C and 0.500 g/dL concentration; * ML_1 samples data have been already reported in a previous work.[2]

Table 2. Most relevant data for the grafted VPyS samples.

	VPyS CuL$_x$					
	$T_g(^{\circ}C)^a$	$T_d(^{\circ}C)^b$	$\eta_{inh}(dL/g)^c$	*Molar Ratio*[d]	$CuO_{calc.}$[e]	$CuO_{exp.}$[f]
VPyS	*131*	*354*	*0.31*	-	-	-
CuL$_1$35	*173*	*302*	*0.21*	*0.254*	*6.27*	*6.17*
CuL$_2$35	*175*	*307*	*0.24*	*0.217*	*5.35*	*5.37*
CuL$_1$60	*208*	*301*	*0.17*	*0.707*	*10.6*	*10.5*
CuL$_2$60	*216*	*305*	*0.21*	*0.604*	*9.18*	*9.27*
	VPyS PdL$_x$					
	$T_g(^{\circ}C)^a$	$T_d(^{\circ}C)^b$	$\eta_{inh}(dL/g)^c$	*Molar ratio*[d]	$\%Pd_{cal..}$[g]	$\%Pd_{exp.}$[h]
VPyS	*131*	*354*	*0.31*	-	-	-
PdL$_1$35	*174*	*340*	*0.31*	*0.232*	*7.65*	*7.95*
PdL$_2$35	*170*	*347*	*0.30*	*0.200*	*6.6*	*7.0*
PdL$_1$60	*217*	*334*	*0.21*	*0.645*	*13.1*	*12.9*
PdL$_2$60	*230*	*332*	*0.22*	*0.558*	*11.3*	*12.0*

[a] Glass transition temperature; [b] 5% Weight loss temperature; [c] Inherent viscosity measured in N,N-dimethylacetamide at 60 °C and 0.500 g/dL concentration; [d] Molar ratio for metal complex fragments referred to pyridine groups; [e] Calculated metal content as CuO; [f] Found metal content as CuO; [g] Calculated metal content as Pd(0); [h] Found metal content as Pd(0).

The ^1H NMR spectra recorded in d_2-dichloromethane solutions on samples of the palladium containing polymers show only broad peaks typical of a polymeric material. The signals correspondent to the ligands are detected in the region between 7 and 8 ppm (those related to the aromatic protons) and in the region between 2 and 4 ppm (those related to the aliphatic protons). The more relevant resonance is the shoulder at about 8.6 ppm due to the protons *orto* to the coordinated pyridinic nitrogen, detectable at about 8.2 ppm for the free pyridinic groups. By integration of this signal versus the signal at about 3.4 ppm, due to the CH_2 groups on the nitrogen of the chromophores, it is possible to evaluate the experimental grafting percentage as being close to the theoretical one.

For both the Pd(II) and Cu(II) grafted polymers series, the experimental chromophore grafting ratio has been determined through thermogravimetric analysis. Cu was determined as CuO, and Pd as Pd(0). On the average, the calculated CuO or Pd(0) contents are in good agreement with the experimental for all the samples (see Table 1 and 2). For Cu(II) VPyS series another test to certify the composition of the grafted polymers was the quantitative analysis of UV-Visible spectra. For this reason the experimental values of the absorbance of the grafted polymers were compared with the theoretical ones, calculated on the basis of the absorbance of the corresponding model complexes (see Table 3).

Table 3. Grafted polymers weight composition from UV-Vis analysis.

	CuL_135 VPyS	**CuL_235 VPyS**	**CuL_160 VPyS**	**CuL_260 VPyS**
$\%_{theo.}$[a]	*35*	*35*	*60*	*60*
$\%_{exp.}$[b]	*35*	*38*	*59*	*57*

[a] theorical chromophore weight percentage. [b] experimental chromophore weight percentage.

DSC curves of all the polymers show only the glass transition signal at temperature higher than the T_g of the host polymer; there is no other glass transition signal related to the free polymeric backbone at lower temperature, due to plasticizing effects of the free complexes. This result confirm that grafting really occurs.

Finally, some regularities in the properties of these materials can be pointed out. All the samples, the metal, the ligand and the polymeric matrix apart, show an increase of the T_g and a decrease of the decomposition temperature on increasing the chromophore weight ratio. Comparing the glass transition temperatures of the samples grafted on the two different polymeric backbones, PVP and VPyS, it is not possible to observe a regular trend. However, the VPyS grafted series nearly always displays a wider range of the T_g values according to the chromophore percentage, on the same metal and ligands. Moreover, the grafted VPyS show, on the average, T_g temperatures lower then the analogous PVP grafted samples, on the same metal, ligands and grafting ratio. So, in the case of VPyS series, it is possible to increase the chromophores weight percentage keeping glass transition temperatures not too high. In fact, in some cases it could be desirable to have quite low glass transition temperatures in order to enhance the efficiency of polar order. We also observed that samples containing palladium always display higher thermal stability than the analogous copper containing polymers. Anyway, all the polymers are thermally stable up to 300 °C. It is remarkable that there is a large temperature range between glass transition and decomposition temperature to carry out the poling process.

The polymers inherent viscosities show a regular trend, as previously observed for the other grafted PVP samples.[1] The viscosities always decrease on increasing the chromophores weight percentage. The X-ray diffraction spectra of all grafted polymers show only broad haloes, thus indicating the amorphous nature of the samples, as already detected by the polarizing optical microscope observation.

All the metallated polymers are soluble in common organic solvents, as N,N-dimethylformamide, 1-methyl-2-pyrrolidinone, dichloromethane. Thin films, obtained by spin-coating technique on glass square supports from 1-methyl-2-pyrrolidinone or 1,1,2,2 tetrachloroethane solutions, and dried in oven at 120 °C for 12 hours, display good homogeneity and transparency. They retain these properties also after annealing in conditions similar to those of the poling process. No phase separation is observed also after several months, at room temperature. Their NLO characterizations (SHG measurements) are in progress.

Conclusions

The employment of a new copolymer as host matrix in the preparation of grafted materials for non linear optics gives improvements in the final properties of the NLO material. The presence of styrene units allows for a higher mobility of the dyes in the polymer and, at the same time, it alleviates the problems related to the hydrophilic behavior of the pyridine groups. However, the material still contains a number of free pyridinic groups that should be large enough for the stabilization of the poling order (as always proved in the case of PVP metallated homopolymers[1]). The range of modulation of some properties, as glass transition temperatures, was enlarged. Both the PVP and the VPyS grafted samples exhibit good properties of high glass transition temperatures, high thermal stability and good solubility. Their films are transparent and homogeneous and appear suitable for nonlinear optical uses.

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